
DETERMINATION OF THE FORMS OF NITROGEN RELEASED IN COAL TAR DURING RAPID DEVOLATILIZATION

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DISCLAIMER

ABSTRACT

The primary objective of this work is to determine the **forms of nitrogen in coal that lead to nitrogen release during devolatilization**. Experiments are to be performed in two existing **laminar flow reactors** available at Brigham Young University, which are both capable of temperatures (up to 2000 K), particle heating rates (10^4 to 10^5 K/s), and residence times (up to 500 ms) relevant to conditions commonly encountered in industrial pulverized coal combustors. The forms of nitrogen in coal, char, and tar samples are analyzed using state-of-the-art techniques, including nuclear magnetic resonance (**NMR**), X-Ray photoelectron spectroscopy (**XPS**), and high resolution **nitrogen-specific chromatography**. These sophisticated analysis techniques are being performed in collaboration with other researchers at BYU, the University of Utah, and industrial organizations. Coals have been obtained as a function of rank, including eight coals from the University of Utah that are to be used in pilot scale tests in support of the DOE Coal-2000 HiPPS (High Performance Power Systems) and LEBS (Low-Emission Boiler Systems) programs. Results from the proposed research are (a) nitrogen release parameters during devolatilization for specific coals pertinent to the HiPPS and LEBS projects, (b) better fundamental understanding of the chemistry of nitrogen release, and (c) a nitrogen release submodel based on fundamental chemistry that may be more widely applicable than existing empirical relationships.

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EXECUTIVE SUMMARY

The primary objective of this work is to determine the forms of nitrogen in coal that lead to nitrogen release during devolatilization. During this reporting period, major progress was made in developing the analytical techniques necessary to identify the forms of nitrogen in coal and coal pyrolysis products. Dynamic nuclear polarization (DNP) techniques were developed and applied to model compounds and coal samples in an effort to improve the signal to noise ratio observed during ^{15}N NMR analyses of coal. The enhancements gained using the DNP technique were measured for model compounds and an Argonne Premium Pocahontas #3 coal sample. These enhancements are currently on the order of 30 times that seen in standard (CP/MAS) ^{15}N NMR experiments for model compounds, but have not yet been realized for coal samples. Current work is focusing on optimizing probe design so enhancements will be observed for coal, char and tar samples.

During this reporting period, a model of nitrogen release as a function of coal type was developed based on the chemical structure of nitrogen in coal. Initial model formulation and evaluation has now been completed. The model successfully predicts the nitrogen release during devolatilization as tar, as light gas (HCN), and the nitrogen that remains in the char. In addition, the model predicts the nitrogen per aromatic cluster in the char, which is measurable by C^{13} NMR spectroscopy combined with elemental analysis. Model predictions agree well with experimental nitrogen release and chemical structure data for a variety of coals and devolatilization conditions. This is the first time that solid-state structural data have been used to help evaluate model predictions, which helps reduce the empiricism of earlier models.

In addition, at the request of industrial collaborators, a brief study was made to see if major pyrolysis gases could be modeled without the computational expense of solving 20 species continuity equations, as in existing models. Preliminary results from this brief study indicate that the species can be calculated in an efficient manner from chemical structure variables using a correlation based on the extent of gas release for different coals. This model seems to work well with a variety of coals for pyrolysis in a wide range of conditions, and therefore may be useful in comprehensive coal combustion models.

INTRODUCTION

Control of emissions of nitrogen oxides (NO_x) from coal combustion systems is becoming a major design and retrofit consideration. Most NO_x in coal combustion systems comes from nitrogen in the fuel, rather than from nitrogen in the air. Practical emission control strategies include burner design strategies (e.g., low NO_x burners), overfire air, reburning, selective non-catalytic reduction (SNCR) using reduction agents such as NH_3 or urea, and selective catalytic reduction (SCR). The order listed also reflects the order of increasing costs for implementation. It is therefore most economically desirable to perform burner modifications to reduce NO_x emissions rather than other control measures.

Low-NO_x burners work on the principle that devolatilized nitrogen species will form N_2 rather than NO_x under locally fuel-rich conditions with sufficient residence time at appropriate temperatures. The amount and form of nitrogen released during devolatilization influence the degree of NO_x reduction attainable using burner design strategies for a given coal. Nitrogen in the char following devolatilization is released by heterogeneous oxidation, and may not be controlled by aerodynamic burner modifications.

The use of comprehensive computer modeling is becoming an efficient screening method in the design of new systems, when based on sound fundamental understanding of the systems to be modeled. Although several empirical relationships for nitrogen evolution from coal during devolatilization have been developed, the fundamental chemistry of coal nitrogen evolution is still not fully understood, and is a weak link in comprehensive coal combustion models used for screening of new systems.

The objectives this work are to perform detailed chemical measurements of the forms of nitrogen in coal, char, and tar. Questions to be answered by this research fall into two categories:

1. Why do low rank coals (i.e., lignites) release as much nitrogen during devolatilization as hva bituminous coals when the tar yields are markedly different?
2. Why do coals of similar rank and elemental composition release different amounts of nitrogen during devolatilization?

Seven tasks are proposed to help answer these two questions:

1. Obtain representative coals being used or considered for use by industry. This includes eight coals from Dr. Pershing at the U. of Utah that will be used in his research for the DOE-HiPPS and DOE-LEBS programs.

2. Analyze parent coals for:
    - elemental nitrogen content
    - extract yield
    - elemental composition of extracts
    - XPS nitrogen form (5-member, 6-member, etc.)
    - ^{15}N NMR spectra

3. Collect char samples in the FFB under 0% post-flame O_2 conditions. Determine the fraction of nitrogen released during pyrolysis at high heating rates and temperatures in the FFB. Also perform XPS and ^{15}N NMR experiments on selected FFB chars.

4. Perform HPCP pyrolysis experiments to collect tar and char samples as a function of residence time and temperature. Determine the fraction of nitrogen released during pyrolysis at high heating rates and temperatures. Also perform XPS and ^{15}N NMR experiments on selected HPCP chars and tars.

5. Perform solvent extractions on parent coals and partially-devolatilized coal chars, saving both extract and residue samples. Analyze residues and extracts for elemental composition. Perform ^{15}N NMR and high resolution chromatography experiments on extracts to look for changes in the forms of nitrogen as a function of coal type and extent of devolatilization.

6. Perform new NMR experiments (i.e., DNP) to better characterize forms of nitrogen in coal, coal char, and tar.

7. Develop a model of nitrogen release as a function of coal type based on chemical forms of nitrogen in coal.

EXPERIMENTAL APPARATUS

This research focuses on the solid and liquid products produced during coal devolatilization. These include coal chars, tars and solvent extraction products of char. To produce the devolatilized products two systems were used: a drop tube reactor (HPCP) and a flat flame burner (FFB). The HPCP has been used to perform moderate temperature experiments (800 to 1200 K) at atmospheric pressures to provide char and tar samples as a function of residence time during devolatilization. The FFB experiments provide char and soot samples from a high temperature, high heating rate environment with products of methane combustion present.

RESULTS AND DISCUSSION

The cost-shared part of this project started on May 1, 1995, and the DOE part started on August 1, 1995. A no-cost extension was granted through April 30, 1999. Accomplishments from May 1, 1998 to October 31, 1998 include:

- Development and evaluation of a nitrogen release model based on chemical structure.
- Initial development of an efficient model of light gas release.
- Further development of the ^{15}N DNP/NMR technique.

Nitrogen Release Model

It is thought that nitrogen is released during primary devolatilization in two ways:[1] (i) nitrogen contained in the aromatic clusters is transported away as tar molecules escape from the char (this is the primary mode of nitrogen release during devolatilization); and (ii) additional nitrogen can be released as light gas (thought to be primarily HCN and NH_3) following the thermal rupture of aromatic rings containing nitrogen heteroatoms (i.e. pyrrolic and pyridinic rings). Several nitrogen release models have been developed based on the following assumptions:[1,2] (i) nitrogen atoms are randomly distributed through the coal's aromatic clusters; (ii) nitrogen atoms contained in the aromatic clusters are transported from the infinite matrix during tar evolution; (iii) ring opening and condensation reactions are negligible (cluster size is not affected by ring opening reactions); and (iv) nitrogen release from the rupture of pyrrolic and pyridinic rings can be adequately described by a first order rate expression with a distributed activation energy function.

The nitrogen release model developed here differs from other existing models in that nitrogen release is partially based on the chemical structure as determined by ^{13}C NMR analysis of the parent coal. Based on the chemical structure of the coal and the devolatilization conditions, the model predicts the amount of nitrogen released with tar, the amount of nitrogen released as light gas by the rupture of pyrrolic and pyridinic rings, and the nitrogen content of the char. Nitrogen released with the tar was modeled by developing a simple scheme to account for the fraction of nitrogen transported with the tar at each time step. Additional nitrogen in the form of light gas from the thermal rupture of pyrrolic and pyridinic rings was modeled by a first order Arrhenius rate equation with a distributed activation energy, as follows:

$$\frac{dN_{site}}{dt} = kN_{site} \tag{1}$$

N_{site} is the dry, ash, free nitrogen content of aromatic sites (an aromatic site is defined as the aromatic portion of a cluster), and k is a first order Arrhenius rate constant that is distributed over a Gaussian probability function based on the extent of nitrogen release.[4] The kinetic parameters, A, E, and σ were empirically fit to best match the experimental data on nitrogen release during devolatilization reported by Fletcher and Hardesty.[3]

It is critical that the initial N_{site} be accurately calculated. The initial value of N_{site} can be determined from ^{13}C NMR measurements of the chemical structure of coal as follows:

$$N_{site_0} = N_{coal}\frac{M_{cl_0}}{M_{site}} \tag{2}$$

where N_{coal} is the dry, ash, free nitrogen content of the coal, M_{site} is the molecular weight per site, and M_{cl_0} is the initial average molecular weight per cluster in the coal as determined by ^{13}C NMR. M_{site} is calculated using measurements of coal structure as determined by ^{13}C NMR according to:

$$M_{site} = M_{cl_0} - (\sigma + 1)M_\delta \tag{3}$$

where $\sigma + 1$ is the total number of attachments per cluster (coordination number) and M_δ is the average molecular weight per side chain.

The nitrogen content of the char can be calculated by converting N_{site} to a per cluster basis as follows:

$$N_{char_i} = N_{site_i}\frac{M_{site}}{M_{cl_i}}, \tag{4}$$

At each time step, the fraction of nitrogen released due to the decay of N_{site} (from the rupture of pyrrolic and pyridinic rings) is calculated, and N_{site}, M_{cl}, and N_{char} are updated.

Results of Nitrogen Release Modeling

Model predictions of nitrogen release compared well with experimental yields for most coals and devolatilization conditions tested. The Chemical Percolation Devolatilization (CPD) model[4] was used to calculate tar and gas yields, as well as the basic chemical structure of the char. Figure 1 compares the nitrogen model predictions with experimentally-determined values of N_{site} and N_{char} for Beulah Zap lignite and Blue #1 coal pyrolyzed by Fletcher and Hardesty[3] at 1050 K and 1250 K maximum gas temperatures at various residence times. Figure 2 compares the predicted and measured values of total mass release and nitrogen release for these same experiments. The experimental data in Figure 1 indicate that under these devolatilization conditions (drop tube with a heating rate of ~ 10^4 K/s) N_{site} decayed very little at the 1050 K condition and began to decay at about 50 ms in the 1250 K condition. The nitrogen release model accurately predicted this trend. The data also show that N_{char} initially increased as aliphatic material was released as light gas, then stopped increasing or began to decrease as light gas release ended and N_{site} decay began. Again, the model accurately predicted this trend for both coals at both conditions.

Predictions of total nitrogen release also compared well with experimental data (Figure 2). It seemed that when total mass release was accurately predicted, nitrogen release was also accurately predicted.

Figure 3 compares total mass release and nitrogen release for five PETC coals pyrolyzed by Fletcher and Hardesty[3] in a flat-flame burner with a heating rate of ~ $5x10^4$ K/s and a maximum gas temperature of ~ 1550 K. Again, model predictions of mass and nitrogen release compared well for most coals. Nitrogen release from Pocahontas #3, a low volatile bituminous coal, at this condition was over-predicted, the cause of which is currently being investigated.

Comparisons have also been performed between model predictions and the drop tube pyrolysis experiments of Chen and Niksa,[5] with excellent agreement.[6] Comparisons with recent BYU pyrolysis experiments also show remarkable agreement, especially with the fraction of nitrogen remaining in the char.

NMR Analysis

Work has continued on obtaining DNP data on coals. Coal samples present a special challenge due to their “lossey” nature (e.g., they are highly conducting). Hence, it is difficult to focus the microwave power efficiently in the sample. We have experienced several major amplifier problems, resulting in significant time delays. The design of the microwave horn antenna and reflector are critical in order to maximize the efficiency of the microwave power. Efforts are now being devoted to optimizing the probe design in order to minimize these difficulties.

FUTURE PLANS

Future plans include performing solid-state ^{13}C (CP/MAS) and ^{15}N (DNP) NMR analyses on the char and tar samples already obtained at the 820 K and 1220 K conditions in the HPCP. These analyses will provide a greatly enhanced knowledge of the chemical structure of char and tar during primary pyrolysis. Additionally, a great deal of information will be gained about the chemical environment of the fuel nitrogen during pyrolysis. Modeling will be completed during the next period, and the results will be submitted for publication.

SUMMARY AND CONCLUSIONS

A model was developed to describe the release of nitrogen during rapid devolatilization. The model was incorporated into the CPD devolatilization model, since the CPD model predicts pyrolysis behavior based on measured chemical structure (rather than empirical representations), and since this model is computationally efficient. The nitrogen release model treats nitrogen release with tar and nitrogen release as light gas from char. The nitrogen model was developed based on chemical structure parameters that are easily calculated in the CPD model and that can be measured using a combination of ^{13}C NMR spectroscopy and elemental analysis. Nitrogen model predictions were demonstrated to agree well with measured nitrogen release for a variety of coals and heating conditions. In addition, the predicted values of the chemical structure of nitrogen (i.e., nitrogen per aromatic cluster site in the char) agree quite well with measured values. The comparisons with chemical structure data are unique, and for the first time justify the model on a mechanistic basis rather than on an empirical basis.

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PUBLICATIONS/PRESENTATIONS RELATED TO THIS CONTRACT

A. Publications

Sponsored by Contract

Genetti, D., T. H. Fletcher, and R. J. Pugmire, "Predicting ^{13}C NMR Measurements of the Chemical Structure of Coal Based on Elemental Composition and Volatile Matter Content," accepted, Energy and Fuels (October, 1998).

Hambly, E. M., T. H. Fletcher, M. S. Solum, and R. J. Pugmire, "Chemical Structure of Coal Tar during Devolatilization Using Solid-State ^{13}C NMR," submitted to the *27th Symposium (International) on Combustion* (December, 1997).

Kelemen, S. R., M. L. Gorbaty, P. J. Kwiatek, T. H. Fletcher, M. Watt, M. S. Solum, and R. J. Pugmire, "Nitrogen Transformations in Coal during Pyrolysis," *Energy and Fuels*, **12**, 159-173 (1998). (partially sponsored by contract)

Watt, M., T. H. Fletcher, S. Bai, M. S. Solum, and R. J. Pugmire, "Chemical Structure of Coal Tar During Devolatilization," *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 3153-3160 (1996).

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Brown, A. L. and T. H. Fletcher, "Modeling Soot Derived from Pulverized Coal," *Energy and Fuels*, **12**, 745-757 (1998).

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B. Presentations

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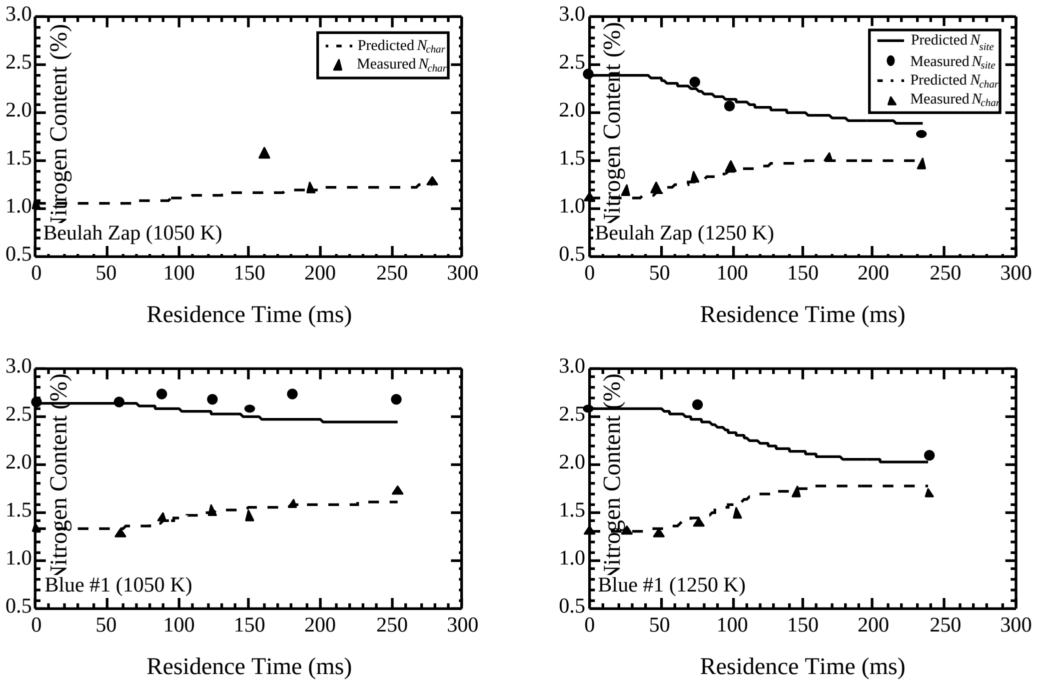

Figure 1. Comparison of N_{site} and N_{char} with model predictions for Beulah Zap and Blue #1 coals. Data reported by Fletcher and Hardesty.[3]

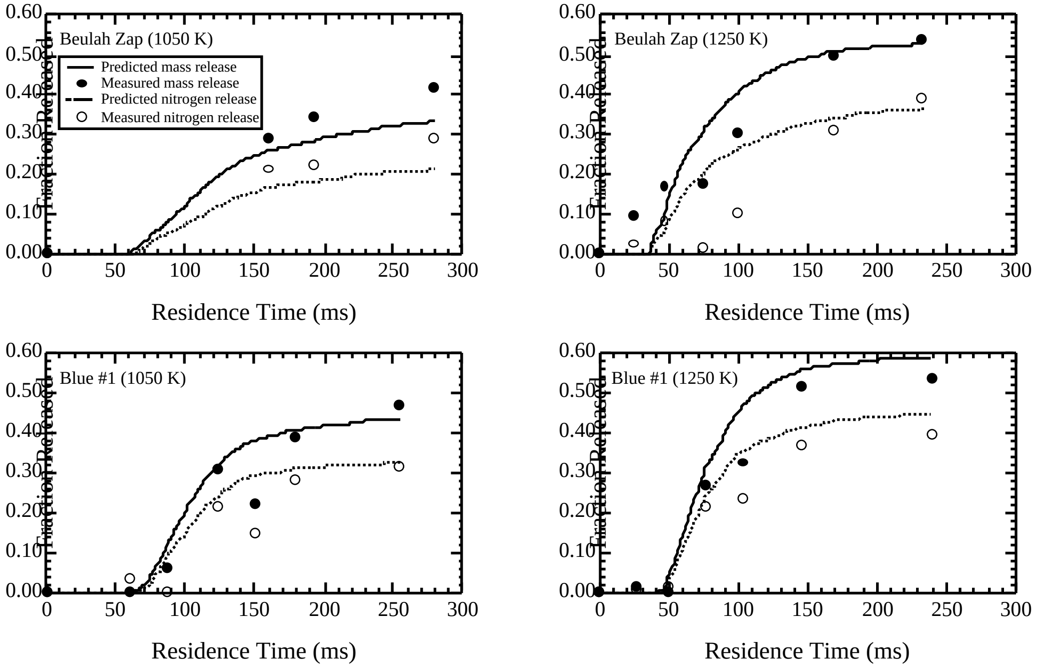

Figure 2. Comparison of total mass and nitrogen release with model predictions for Beulah Zap and Blue #1 coals. Data reported by Fletcher and Hardesty.[3]

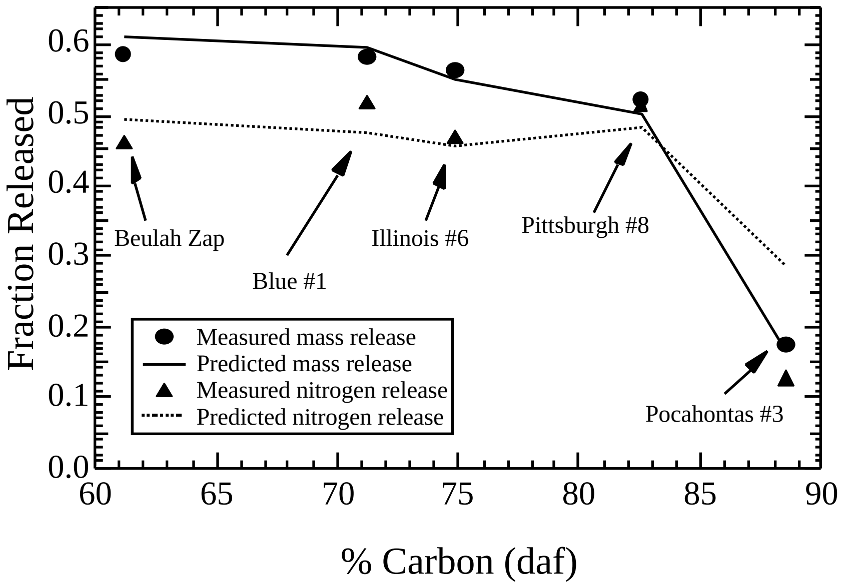

Figure 3. Comparison of predicted and measured mass and nitrogen release for five PETC coals pyrolyzed by Fletcher and Hardesty.[3]